EFFICIENCY OF THE EXTRUSION PROCESS OF THERMOPLASTICS MODIFIED WITH BLOWING AGENT

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ABSTRACT

Extrusion process is one of the most popular polymer processing method. It allows to produce different types of shapes e.g. pipes, cables, plates, nets, films, coating, bars. This kind of shapes are usually made from typical thermoplastics materials like PVC, HDPE, LDPE, PP, PS, which characterizes solid physical structure. Nowadays, the most popular processing method is modification of plastic material with different types of agents. The modification consists of adding auxiliary agents takes place through the introduction of these materials during plastic processing or directly in its production. These measures include the modifiers primarily to improve physical toughness, thermal formability or ductility. It could be flame retandant agent, flow agent, stabilizing agent, curing agent, filler, release agent, nucleant agent and blowing agent (porophor).

The growing interest in porous plastic materials and their means of production led to the formation of a new method of processing, which is the microcellular extrusion process. This extrusion method of thermoplastics in recent years is one of the fastest growing methods of polymer processing. The aim is to obtain different microporous shapes and coatings with reduced density, without subsidence on the surface of extrudate and exhibiting minimal shrinkage while maintaining the similar nature of the products of extruded by a conventional method.

Continuous development of microcellular extrusion process and the design elements comprising the technological lines creates new opportunities for research.

Article presents a study of microcellular extrusion process and its efficiency during modification with blowing agent in the form of microspheres.

1. INTRODUCTION

The extrusion process of microcellular thermoplastic is the subject of scientific research, yet little developed, the results have been presented only in few publications. This process is in recent years, one of the fastest growing methods of processing these materials. Its aim is to obtain profiles and microporous coatings with reduced density and subsidence at the surface without marc and exhibiting minimal shrinkage, while maintaining similar properties to the extruded products by a conventional method. Microcellular extrusion process consists in adding to the input material the blowing agent, a gas, which under appropriate conditions of the extrusion process is expanded, and increase its size several times.

As a result of processing a received product have two-phase structure, changed from the solid to microporous. The new structure of the material can be microporous throughout its cross section or have a solid outer layer and a microporous core. To achieve this its important to enter the gas into the plastic in the suitable form and time. The formation of pores occurs in the last zone of the extruder plasticizing system [8].

Change in microstructure of the material takes place through appropriate selection of extrusion conditions, mainly temperature distribution in the various zones of the plasticizing unit and zones of extrusion head, as well as a result of construction machinery and tools used in this process [9]. The carefully selected input material, blowing agent and nucleant, the extrusion process conditions and design tools allow to obtain products of the new modified properties.

Important role in the microcellular extrusion process plays temperature in different zones of the extruder plasticizing system and extrusion head zones. Its value should be close to the distribution temperature of blowing agent, but must be chosen so that the blowing agent was decomposed in the relevant zone of plasticizing extruder. This increases the viscosity of the processed material, which prevents expansion of the gas contained in the material flowing through the extrusion head. Decrease or increase porosity of the product structure is done by gradual dosing of blowing agent and adjustment screw rotational speed of the extruder [1].
The stream of plastic with blowing agent is transported under pressure to the extrusion head. The value of this pressure should be large enough that the gas inside the porophor not be spun off as a separate phase in the stream of material. As a result of shear stress in flowing plastic material barrier separating the gas bubbles would be destroyed mechanically. Plastic pressure grows extensively in the plastic along the extruder plasticizing system, slightly declining in the last part of the first zone and the boring head and then drops sharply at the nozzle head, up to atmospheric pressure.

The gas pressure initially increases quite extensively, although it is much smaller than the pressure of the material, then more slowly until the end of the boring head nozzle and outside, where a sudden drop in pressure [3].

In the process of extrusion profiles and coatings, shape and dimensions of the cross section gives a pre-brewing extrusion head, taking into account the effect of shrinkage Barus phenomena and processing, but it is not yet stable system. In order to obtain a uniform micro-brewing, devoid of micropores and external surface of the required size and shape, it becomes necessary to perpetuate it through the rapid cooling and solidification in the process of calibration [5].

Used in the microcellular extrusion process lines calibration device are designed to cool the residue to such a temperature that ensures the stability of shapes and sizes. The selection of calibrator determines the calibration method, a solution, design and method of cellular process. Internal calibration involves performing a open cross-section of extrudate after cooling the calibrator rod of a certain diameter and length and with a suitable clamp. Marc for the stem clamp calibration is due to contraction during cooling of extrudate. However, during external calibration of the extrudate after leaving the extrusion head is made by cooling sizing sleeve. As a result of the temperature difference between the extrudate and the surface of the cooling sleeve consolidation of the profile shape and dimensions takes place [7].

Microcellular extrusion process is applied during the manufacture of various types of shapes, in which there is a need for a significant reduction in the density of a product or change the selected physical properties, especially mechanical or utilitarian bagasse [1, 3, 8].

1.1. Microcellular extrusion methods

Depending on the structure of the resulting extrudate divided into the following microcellular extrusion method [2]: free cellular method, inside cellular method, partial cellular method, co-extrusion cellular method.

During free cellular method the entire cross section of extrudate have a porous structure, whose growth is limited by the cooling profile. This is due to the considerable distance between the extrusion head a calibrating device. As a result, this method produced extrudates are cellular in the whole section of product. With this method it is necessary to use a boring head nozzle with smaller cross-section relative to the channel cross-section of the calibrator.

Extrusion conducted by the inside cellular method, is also called a method Celluka. In this method, followed by intensive cooling of extrudate in the calibrator over its entire surface immediately after leaving the nozzle. This is to give the desired shape of extrudate by inhibiting proliferation of blowing agent and to avoid the formation of porous structure on the profile surface. As a result of this method the porous extrudate with solid outer layer is obtained. During cellular extrusion by inside method the external dimensions are identical between the nozzle exit from the boring head and the entrance to the device calibration. The intensity of cooling in this case determines the thickness of the surface layer of solid extrudate, because during this process on the surface do not form pores. By contrast with the free cellular method pore growth is increased by a greater distance between the extrusion head and a calibrator.

Preparation of porous extrudate is also possible through a combination of methods porowania free and Celluka. This method is called partial cellular method and allows the extrusion of sections with the outer layer partially solid. In this case, extensive cooling of extrudate occurs in a particular part of it, while the remainder is freely pore [10].

Foaming extrusion process may also be made using the co-extrusion cellular method. It enables the production of multilayer profiles, in which one layer is porous and the remaining solid. This process is carried out on standard lines, boring, but the need is to equip them with special heads, boring and longer calibration. The thickness of the solid outer layer of the resulting extruder head design can be adjusted, namely by moving the nozzle in the direction of one of the extrudate surface increases the intensity of cooling of the surface, therefore, the outer layer is formed thicker solid.

Depending on the cellular extrusion method used and the amount of blowing agents, extruded shapes and porous coatings have different properties. The products obtained by the inside method have higher hardness, resistance to light and atmospheric conditions and surface roughness. Whereas the elements produced by free method may have a greater degree of porosity.

1.2. Blowing agents

In order to properly carry out the microcellular extrusion process is important the proper selection of blowing agents. Type of porophor determines its decomposition temperature, material processed and the processing conditions. It is important that the temperature distribution of blowing agents was higher than the melting point of the material being processed, but lower than the temperature of extrusion of the this material. A further criterion for the selection of blowing agents is the method of processing and machinery and equipment used in the selected process. Porous material in a plastic state, as found in the plasticizing extruder and extrusion head is not yet stable system, as a result of surface tension at the interface: material - gas and diffusion, reducing the number of pores in the material, but increase their sizes what is the undesirable result. The resulting pores increase in time to reach a balance between gas pressure and surface tension of the processed material. The preferred structure of the material with small pores, it acts in the final formation by cooling as quickly as possible. Blowing agents are in the process of extrusion of the same factors as the material being processed, it is heating, compression, homogenized, and transportation, even before the passage of gas. Inert gases and low boiling liquids may be subject to dissolution in the plasticised material, with the blowing agent dissolution rate increases with increasing mixing intensity and gas pressure.

Blowing agents applicable in the extrusion process, is divided into traditional, though not too closely, the physical and chemical [3]. This division shall be carried out because of the way of gas evolution. Physical blowing agents during the cellular process not change its chemical structure, but only the state. They are, therefore, liquids or gases dissolved under pressure in the material, which after raising the temperature and lowering the pressure evaporate or emit in the form of bubbles. To this group belong to organic liquids of low boiling point: primarily aliphatic hydrocarbons and chlorofluorocarbons them. Chemical blowing agents operate in a similar way as physical blowing agents, but the gaseous products resulting pores are formed from the decomposition of the material. They are divided into inorganic and organic.

Porophors used during the cellular process may have exothermic or endothermic decomposition characteristics [6]. But so far used in the extrusion process are exothermic blowing characteristics of the distribution. This can cause local overheating and the formation of an irregular porous structure of the product. Started blowing agent decomposition takes place spontaneously, even after cutting off the supply of energy. Therefore, the products of this type of porous measures must be cooled to prevent distortion and maintain proper pore structure. The main representatives of this group are hydrazides for example sulfohydrazyd and azo compounds such as azodicarbonamide.

In the case of the porophors with endothermic nature of the distribution, the gas expansion during processing ends abruptly at the end of the energy supply. The use of such blowing agents significantly reduces cooling time of the product. Representatives of this group are among bicarbonates, for example, sodium bicarbonate and ammonium acid.
At present was introduced to the market a new blowing agent in the form of polymer capsules called microspheres, filled with gas from a group of hydrocarbons, such as isobutane, isopentane, isooctane. The microspheres are endothermic nature of decomposition, the thermal energy charge for plasticizing the capsule and the change of state from liquid hydrocarbon in volatile. Under the influence of a certain temperature microspheres increase in size about 50 times. The microspheres form a microporous structure, providing a lower density of extrudate while retaining microscopic cells, closed and homogeneous in size. Microspheres by weight of a product offer tangible economic benefits, also modify other properties, such as susceptibility to compression, the ability to recover the original shape of a product, absorbing vibration and electro-beneficial properties and thermal insulation. The spherical shape is one of the unique features that distinguish this agent from other porophors [4].

During the growth of the barrier properties of the microspheres act to prevent the leakage of gas and a combination of individual capsules with each other. There are several types of microspheres, which are selected depending on the range of processing temperatures and dimensions of the microspheres after expansion.

2. EXPERIMENTAL

Modified PVC extrusion process was conducted in a laboratory extrusion technological line of the shapes in the Department of Polymer Processing, Lublin University of Technology. During the process single-screw extruder T-32-25, provided with a core extrusion head with bar extrusion nozzle was used. The process was performed by free cellular method in order to obtain the free and the maximum growth of microspheres in PVC. Extrusion process was carried out in the revised processing conditions (Table 1) developed on the basis of preliminary studies.

As the input plastic the plasticized PVC Alfavinyl GFM/4-41 TR was used. The plastic was modified with blowing agents in the form of microspheres Expancel 930 MB 120 which is a mixture of microspheres (65%) and EVA copolymer. Blowing agent was dosed at levels from 0% to 2.5% (at 0.5%).

Process was carried out by changing the screw rotating speeds for each content of blowing agent.

Table 1. Processing conditions of plastified PVC modified with blowing agent

Zones of plasticizing system and extrusion head	I	II	III	IV	V
Processing temperature of solid PVC, °C	120	130	140	150	160
Processing temperature of PVC with blowing agent, °C	100	110	120	130	140
Screw rotational speed, rpm	45	61	78	94	111

3. RESULTS

As a result of a modified PVC extrusion process with blowing agent residue in the form of a rod with a diameter of 8 mm was obtained. Physical structure of extrudate was microporous throughout its cross section and characterized by different porosity depending on the used variable factors. An example of the appearance of the structure of the resulting extrudate is shown in Figure 1.

Figure 1. Physical structure of microcellular PVC extrudate with 2.5% content of blowing agent extruded with 78 rpm of screw rotational speed

In the course of the extrusion of PVC modified with microspheres of measurements of mass of measuring length, time of extruded measuring length and the temperature of of the extrudate leaving the extrusion nozzle head were performed. They allowed to determine the mass and volumetric flow rate of extrudate from the extrusion head, Barus phenomena and distribution of temperature on the surface of the microcellular extrudate obtained.
Selected results of the modified PVC extrusion process with blowing agent in the form of diagrams was presented on Figures 2÷5.

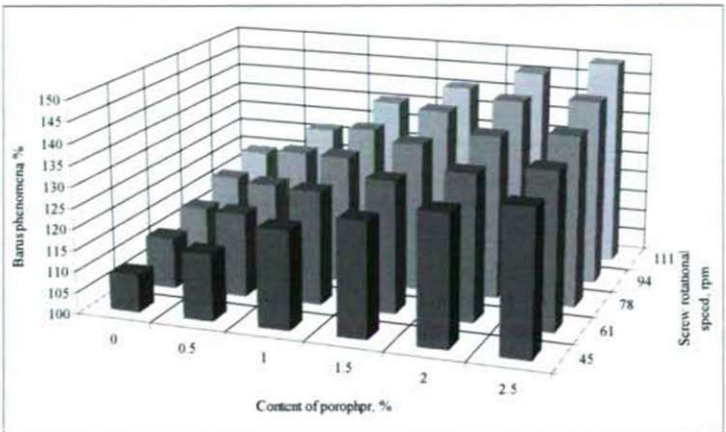

Figure 2. Dependence of Barus phenomena of microcellular PVC extrudate on content of blowing agent and screw rotational speed

The measure of Barus phenomena is the Barus number. Its value has increased in direct proportion with the increase of screw rotational speed regardless of the means of blowing agent. This value also increases gradually and steadily with increasing content of porohor from 0% to 1.5% by mass. After exceeding this value is observed decrease of the Barusa number, which may be due to a weaker expansion of the microspheres in the process, due to the large amount dispensed blowing agent.

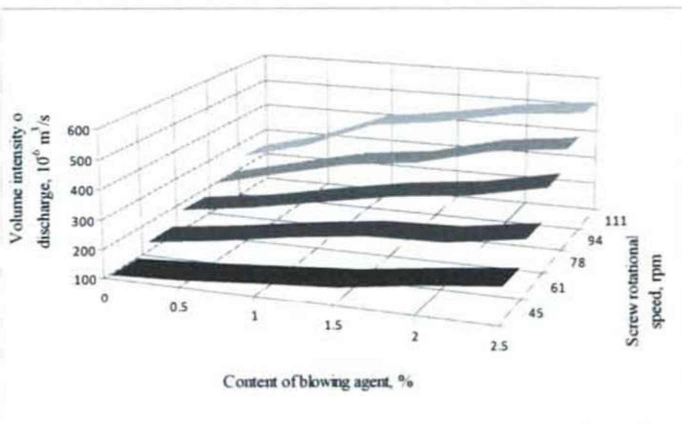

Figure 3. Dependence of volume intensity of discharge of extrudate on content of blowing agent and screw rotational speed

In the whole range of increasing screw rotational speed and increasing the blowing agent dosage, significantly increases the volumetric flow rate of extrudate from extrusion head. At the lowest rotational speed equal to 45 rpm value of the intensity of the solid material (0%) is 100 10-6 m3/s, while the dosage of microspheres in an amount of 2.5 % increases up to 219 10-6 m3/s. The results showed that the intensity of the bands at fixed screw rotational speed rate is directly proportional to the screw rotational speed and increases with increasing the content of the blowing agent in the polymer material. This increase is more intense, while increasing the rotational speed of the screw and increases the amount dispensed porophor.

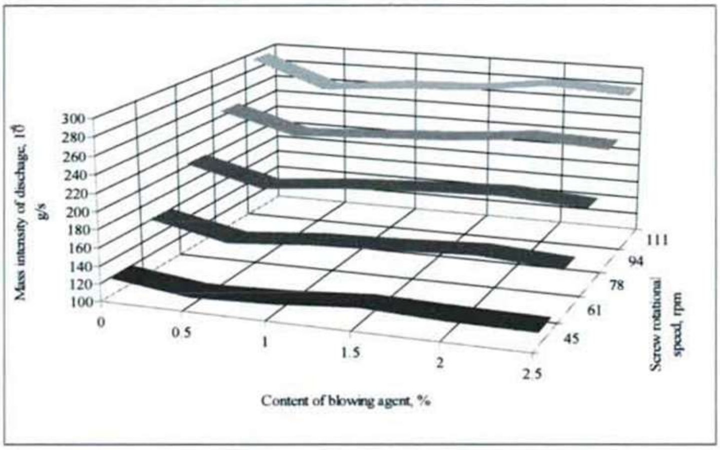

Figure 4. Dependence of mass intensity of discharge of extrudate on content of blowing agent and screw rotational speed

Mass flow rate of extrudate in assistive technologies etc. depends on both the content of blowing agent and the screw rotational speed. At the same time examined the relationship changes slightly in the permitted ranges of values of variable factors. Obtained results bagasse mass flow rate of PVC modified with microspheres showed that the intensity is greater changes under the influence of screw rotational speed increment. In each case considered, this effect is not as significant as the volume flow rate.

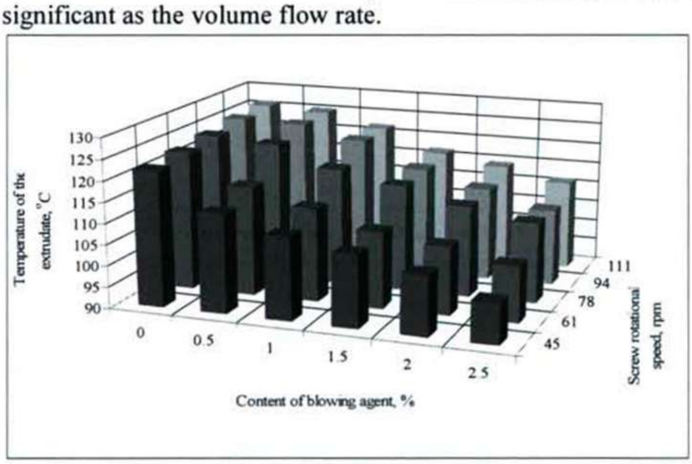

Figure 5. Dependence of temperature of microcellular extrudate on content of blowing agent and screw rotational speed

With increasing dosage of blowing agent center temperature of the material leaving the extrusion nozzle head has decreased, and in the dosage range investigated was a decrease of 15°C. At the same time it can be assumed that the greatest drop in temperature is observed using a dosage amount of 0.5% of blowing agent. When increasing porophor dosage of 1.5% above the masses. temperature of the extrudate was some stabilization at around 130°C. When increasing the screw rotational speed above 78 rpm the temperature of extrudate increased for small content of porophor between 0.5 and 1 %. and its fall to the content above 1.5 % of microspheres.

4. CONCLUSIONS

PVC modification with the blowing agent in the form of microspheres resulted in significant changes in the extrusion process. The changes are caused by a fundamental change in the physical structure and a decrease in the extrudate density. Admitted to the study of the characteristics of the microcellular extrusion process allowed closer and more comprehensive knowledge of the impact of modifying material with the blowing agent in the form of microspheres on the course and efficiency of the process.

As the screw rotation speed and the content of blowing agent in PVC plasticized increases volumetric and mass flow rate of extrudate from the extrusion head, as well as the Barus phenomena. This increase is mainly due to hyperplasia of the microspheres, resulting in widening stream of material flowing from the extrusion head. Research microcellular extrusion of PVC modified with blowing agent in the form of microspheres showed a significant influence selection of the conditions of this process on its course. It is first necessary to determine the appropriate value and the temperature distribution in the system plasticizing system of the extruder and extrusion head, different than the extrusion of the same material but solid.

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